ARCHIVES

GEORGIA TECH RESEARCH INSTITUTE

GEORGIA INSTITUTE OF TECHNOLOGY

ATLANTA, GEORGIA

PROJECT A-128

STATUS REPORT NO. 1-9

DETERMINATION OF MOLECULAR CONSTANTS BY MICROWAVE AND RADIOFREQUENCY SPECTROSCOPY

TECHNICAL REPORT NO. 1

MICROWAVE SPECTRUM AND MOLECULAR CONSTANTS OF NITROSYL BROMIDE

BY

T. L. WEATHERLY AND JOEL Q. WILLIAMS

DEPARTMENT OF ARMY PROJECT NO. 599-01-004
OOR PROJECT NO. 1016
CONTRACT NO. DA-01-009-ORD-353

1953-1955

GEORGIA INSTITUTE OF TECHNOLOGY
ATLANTA, GEORGIA

SCHOOL OF PHYSICS

Status Report No. 1

DETERMINATION OF MOLECULAR CONSTANTS BY MICROWAVE AND RADIOFREQUENCY SPECTROSCOPY

Contractor:-

Georgia Tech Research Institute
Research Building
Georgia Institute of Technology
Atlanta, Georgia

Period:-

1 October 1953 to 31 December 1953

Project No:-

OOR 1016

Contract No.:-

DA-01-009-ORD-353

Submitted by:-

T. L. Weatherly
Associate Professor

Joel Q. Williams
Assistant Professor

Approved:-

Herschel H. Cudd, Director
Engineering Experiment Station

Status Report No. 1

Determination of Molecular Constants
by
Microwave and Radiofrequency Spectroscopy

Contract No. DA-01-009-ORD-353

Personnel: During the quarter ending 31 December 1953, the co-directors, Joel Q. Williams and T. L. Weatherly of the School of Physics, have devoted one-third of their time to research under this contract. Mr. James H. Mauldin a graduate student in physics, has shown an interest in this work and will be employed as a graduate assistant, effective January 1, 1954. He will be paid $111.11 per month for one-third time.

Fiscal: Expenditures during the quarter were as follows:-

Salaries and Wages....	$1134.45
Overhead	522.41
Supplies	16.08

Microwave Spectroscopy: The microwave spectrograph has been assembled and tested on the N_2O absorption line at 25,123 Mc. Some delay has been encountered in the delivery of a microwave frequency standard ordered by the School of Physics March 30, 1953. Meanwhile some time has been devoted to the testing of absorption type wavemeters which have just recently been constructed.

Radiofrequency Spectroscopy: A search for nuclear quadrupole resonance has been made in twenty-one chlorine compounds in the 20 to 40 Mc region. Absorption lines were detected in five of these substances. Results of this work will be reported at a later date.

GEORGIA INSTITUTE OF TECHNOLOGY
ATLANTA, GEORGIA

CHOOL OF PHYSICS

Status Report No. 2

DETERMINATION OF MOLECULAR CONSTANTS BY MICROWAVE AND RADIOFREQUENCY SPECTROSCOPY

Contractor:-
Georgia Tech Research Institute
Research Building
Georgia Institute of Technology
Atlanta, Georgia

Period:-
1 January 1954 to 31 March 1954

Project No:-
OOR 1016

Contract No.:-
DA-01-009-ORD-353

Submitted by:-

T. L. Weatherly
Associate Professor

Joel Q. Williams
Assistant Professor

Approved by:-

Paul K. Calaway, Director
Engineering Experiment Station

Status Report No. 2

Determination of Molecular Constants
by
Microwave and Radiofrequency Spectroscopy

Contract No. DA-01-009-CRD-353

Personnel: During the quarter ending 31 March 1954, the co-directors Joel Q. Williams and T. L. Weatherly of the School of Physics and James H. Mauldin, Graduate Assistant, have devoted one-third of their time to research under this contract.

Fiscal: Expenditures during the quarter were as follows:

Salaries and Wages.....	$1466.64
Overhead.....	667.32
Supplies.....	1189.73
Freight and Express.....	6.10
Total.....	$3329.79

Microwave Spectroscopy: During this quarter much time has been spent in becoming acquainted with the equipment. Absorption lines of previously reported molecules were observed on the oscilloscope and were recorded using a phase sensitive detector and recording milliammeter. The following molecules were used: nitrous oxide, acetone, chloroform, and phosphorus oxychloride. These molecules provided eleven known absorption lines which were used to calibrate two absorption type wavemeters between 24,000 Mc and 40,000 Mc. We have been assured that the microwave frequency standard (ordered by the School of Physics, March 1953) will be delivered in a few weeks.

Radiofrequency Spectroscopy: Nuclear quadrupole resonances have been detected in the chlorine compounds listed below:

1 - Chloro - 2,4-dinitrobenzene	37.796 Mc
4 - Chloro - 3,5-xylenol	34.348 Mc
	34.415 Mc
Ethyl trichlorosilane	18.756 Mc
	18.842 Mc
	18.865 Mc
Ethyl Chloroformate	33.858 Mc
Ethyl Trichloroacetate	40.200 Mc
	40.339 Mc

Measurements on the first three of these compounds were reported in a Letter to the Editor of the Journal of Chemical Physics accepted in January 1954. After improvement of the spectrograph the resonance frequencies for the last two compounds were confirmed and reported in a second Letter to the Editor accepted in March 1954.

GEORGIA INSTITUTE OF TECHNOLOGY
ATLANTA, GEORGIA

SCHOOL OF PHYSICS

Status Report No. 3

DETERMINATION OF MOLECULAR CONSTANTS BY MICROWAVE AND RADIOFREQUENCY SPECTROSCOPY

Contractor:-

Georgia Tech Research Institute
Research Building
Georgia Institute of Technology
Atlanta, Georgia

Period:-

1 April 1954 to 30 June 1954

Project No:-

OOR 1016

Contract No:-

DA-01-009-ORD-353

Submitted by:-

T. L. Weatherly
Associate Professor

Joel Q. Williams
Associate Professor

Approved by:-

Paul K. Calaway, Director
Engineering Experiment Station

Status Report No. 3

Determination of Molecular Constants

by

Microwave and Radiofrequency Spectroscopy

Contract No. DA-01-009-ORD-353

Personnel: During the quarter ending 30 June 1954, the Co-directors, Joel Q. Williams and T. L. Weatherly of the School of Physics, and James H. Mauldin, Graduate Assistant, have devoted one-third of their time to research under this contract.

Fiscal: Expenditures during the quarter were as follows:

Salaries and Wages	$1467.02
Overhead	667.63
Supplies	448.84
Freight and Express	6.10
Travel	74.75
Total	$2664.34

Microwave Spectroscopy: Samples of NOBr have been prepared by mixing gaseous bromine and nitric oxide. This mixture was then distilled to increase the concentration of NOBr. The sample was allowed to flow into the Stark cell and a search for absorption lines was made using different static pressures. No absorption lines have been found using this technique and it is assumed that the gas dissociates quickly at low pressure in the Stark cell. Arrangements have just been made to allow the sample to enter the cell at one end and flow through in a continuous stream. A search for absorption lines using this technique will begin immediately.

Plans for a high voltage square wave generator, for the Stark modulating voltage, have been adopted and parts have been ordered. The construction and testing of this apparatus has been assigned to Mr. James H. Mauldin to be used as the basis for a master's thesis.

The microwave frequency standard has been given a preliminary test and returned to the builders for a few changes.

Radiofrequency Spectroscopy: Nuclear quadrupole resonance for Cl^{35} has been detected in the following compounds at liquid nitrogen temperature:

m-Dichlorobenzene	34.80
	34.871
	35.027
1-Chloro-3-nitrobenzene	35.457
1-Chloro-2-fluorobenzene	36.294
p-Toluenesulfonyl Chloride	32.457
2,5-Dimethylbenzenesulfonyl Chloride	32.265

The first two of these were reported earlier by C. Dean and R. V. Pound [J. Chem. Phys. 20, 195 (1952)] at higher temperatures and are of interest for a more complete determination of the temperature dependence of the quadrupole resonances.

GEORGIA INSTITUTE OF TECHNOLOGY
ATLANTA, GEORGIA

CHOOL OF PHYSICS

Status Report No. 4

DETERMINATION OF MOLECULAR CONSTANTS BY MICROWAVE AND RADIOFREQUENCY SPECTROSCOPY

Contractor:-
Georgia Tech Research Institute
Research Building
Georgia Institute of Technology

Period:-
1 July 1954 to 30 September 1954

Project No:-
OOR 1016

Contract No:-
DA-01-009-353

Submitted by:-

T. L. Weatherly
Associate Professor

Joel Q. Williams
Associate Professor

Approved by:-

Paul K. Calaway, Director
Engineering Experiment Station

Status Report No. 4

Determination of Molecular Constants

by

Microwave and Radiofrequency Spectroscopy

Contract No. DA-01-009-ORD-353

Personnel: During the quarter ending 30 September 1954, the Co-directors Joel Q. Williams and T. L. Weatherly of the School of Physics have devoted full time to research under this contract. Mr. James H. Mauldin, Graduate Assistant, worked approximately one-half time. The remainder of his time was spent on active duty with the Navy.

Fiscal:- Expenditures during the quarter were as follows:

Salaries and Wages.....	$4070.98
Overhead.....	1852.30
Supplies	315.54
Total.....	$6238.82

Microwave Spectroscopy: The investigation of the microwave spectrum of nitrosyl bromide was continued. Due to the instability of this compound some difficulty was encountered in preparing the sample and introducing it into the microwave absorption cell at the low pressure required to detect rotational lines. Several samples were prepared by mixing gaseous bromine and nitric oxide in appropriate proportions and a search for absorption lines was carried out while this mixture was allowed to flow through the cell. After many trials spectral lines were detected by following the procedure outlined below.

Nitric oxide and bromine were mixed in a 2 to 1 ratio until the pressure of the mixture was one atmosphere. (The equilibrium concentration of NOBr increases with pressure). The gas was then frozen with liquid nitrogen and the excess nitric oxide pumped off. The remaining solid was then allowed to sublime and flow through

a microwave absorption cell cooled to dry ice temperature. In this way the fifty seven spectral lines listed in Table I were detected.

These lines fall into groups separated by approximately 6,400 Mc. The rotational quantum numbers J involved in each transition have been identified by comparing the observed spectrum with that computed on the basis of the bond distances and angle determined by electron diffraction. (Ketelaar, J.A., and Palmer, K.J., J. Am Chem. Soc. 56 2629(1937).The computed and observed spectra have the same general character, however, the computed spectrum is shifted slightly to lower frequency. The spectrum is complicated by the presence of two bromine isotopes and a large bromine quadrupole coupling. In spite of this, the prospects for a complete analysis appear to be good.

Most of the material for the high voltage square wave generator has been obtained and Mr. Mauldin has already begun the construction of this Stark voltage generator.

Our microwave frequency standard was used to measure some of the $J = 2 \longrightarrow 3$ transitions. However, its output power needs to be increased so that it will be more useful at higher frequencies, and it was returned to the builders.

Radiofrequency Spectroscopy: An attempt has been made to determine the pure nuclear quadrupole spectrum of a number of inorganic chlorine compounds. The chlorine bond in such molecules is considerably less covalent in nature than that in the organic compounds previously studied. As a result quadrupole resonances would occur at lower frequency. A knowledge of the resonance frequency would be useful in predicting the percent covalency of such a bond. Up to the present, however, no spectral lines have been found in this type of compound.

TABLE I. Frequencies of observed absorption lines of NOBr given in megacycles per second.

J = 2 ⟶ 3	J = 3 ⟶ 4	J = 4 ⟶ 5
21,611.8±0.5*	28,700	35,870
21,630.0±0.5*	28,820	36,030
21,745.4±0.5*	28,825	36,280
21,769.8±0.5*	28,980	36,420
21,835.8±1*	29,010	36,480
21,852.3±0.5*	29,020	36,630
21,860.1±0.5*	29,085	36,710
21,875	29,120	36,810
21,910	29,130	36,830
21,970	29,200	37,100
21,985	29,260	
21,990	29,310	
22,000	29,320	
22,060	29,325	
22,087.7±0.5*	29,330	
22,107.8±0.5*	29,350	
22,150	29,390	
22,170	29,430	
22,225.6±1*	29,460	
22,251.3±1*	29,470	
22,300	29,505	
	29,510	
	29,515	
	29,630	
	29,650	
	29,660	

*These frequencies were measured by frequency standard. All others were measured by absorption type wavemeter with error ± 15 mc.

GEORGIA INSTITUTE OF TECHNOLOGY
ATLANTA, GEORGIA

CHOOL OF PHYSICS

Status Report No. 5

DETERMINATION OF MOLECULAR CONSTANTS BY MICROWAVE AND RADIOFREQUENCY SPECTROSCOPY

Contractor:-
Georgia Tech Research Institute
Research Building
Georgia Institute of Technology

Period:
1 October 1954 to 31 December 1954

Project No:-
OOR 1016

Contract No:-
DA-01-009-353

Submitted by:-

T. L. Weatherly
Associate Professor

Joel Q. Williams
Associate Professor

Approved by:-

Paul K. Calaway, Director
Engineering Experiment Station

Status Report No. 5

Determination of Molecular Constants
by
Microwave and Radiofrequency Spectroscopy

Contract No. DA-01-009-ORD-353

Personnel: During the quarter ending 31 December 1954, Joel Q. Williams and Thomas L. Weatherly, the Co-directors and James H. Mauldin, Graduate Assistant, have devoted one-third time to research under this contract. Mr. Donald F. Eagle, a graduate student in physics, has shown an interest in this research and it is anticipated that he will take part in the project during the quarter beginning January 1, 1955.

Fiscal: Expenditures during the quarter were as follows:

Salaries and Wages	$1706.40
Overhead	776.41
Supplies	586.92
Freight and Express	10.08
Total	$3079.81

Microwave Spectroscopy: The microwave spectrum of nitrosyl bromide has been further investigated. Frequency measurements have been made on all the lines of the $J = 2 \rightarrow 3$ group. An analysis of this group has been made giving the molecular constants listed below.

Rotational Constants	$NOBr^{79}$	$NOBr^{81}$
A	83,730 $\pm$ 200 Mc	83,460 $\pm$ 200 Mc
B	3,746.78 $\pm$ .25	3,722.26 $\pm$ .25
C	3,586.29 $\pm$ .25	3,563.34 $\pm$ .25
Quadrupole Coupling		
$(eqQ)_{Br}$	429.5 $\pm$ 2.6 Mc	358.9 $\pm$ 2.2 Mc

The spectrum computed on the basis of these constants for the $J = 2 \longrightarrow 3$ transition is compared with the observed spectrum in Table I. The agreement of the calculated and observed spectra is good, however we feel that some improvement may be possible.

Table I. The calculated and observed spectra for the $J = 2 \longrightarrow 3$ transition.

	Calculated	Observed
$NOBr^{79}$	21,748.22 Mc	21,748.46 Mc
	21,772.64	21,772.12
	21,972.07	21,973.04
	21,993.61	21,993.64
	21,999.69	22,000.44
	22,017.53	22,017.24
	22,068.66	22,070.14
	22,229.53	22,229.67
	22,253.56	22,253.27
$NOBr^{81}$	21,609.80	21,609.03
	21,630.20	21,629.93
	21,834.21	21,835.72
	21,852.02	21,852.02
	21,857.28	21,859.72
	21,872.00	21,870.43
	21,914.92	21,915.86
	22,086.49	22,085.27
	22,106.57	22,106.87

The interatomic distances computed from these tentative rotational constants are:

$$Br - N = 2.23 \pm .14 \ A^\circ$$

$$N - O = 1.06 \pm .18 \ A^\circ$$

$$Br - O = 2.76 \pm .12 \ A^\circ$$

A more complete analysis of the spectrum may result in changes in these distances.

Mr. Mauldin is proceeding with the construction of the high voltage square wave generator for the stark modulation. Some delay has been encountered in obtaining pulse transformers for this unit, but we expect their delivery in January.

GEORGIA INSTITUTE OF TECHNOLOGY
ATLANTA, GEORGIA

SCHOOL OF PHYSICS

Status Report No. 6

DETERMINATION OF MOLECULAR CONSTANTS BY MICROWAVE AND RADIOFREQUENCY SPECTROSCOPY

Contractor:--

Georgia Tech Research Institute
Research Building
Georgia Institute of Technology
Atlanta, Georgia

Period:-

1 January 1955 to 31 March 1955

Project No:-

OOR 1016

Contract No:-

DA-01-009-ORD-353

Submitted by:-

T. L. Weatherly
Associate Professor

Joel Q. Williams
Associate Professor

Approved by:-

Paul K. Calaway, Director
Engineering Experiment Station

Status Report No. 6

Determination of Molecular Constants

by

Microwave and Radiofrequency Spectroscopy

Contract No. DA-01-009-ORD-353

Personel: During the quarter ending 31 March 1954, Joel Q Williams and Thomas L. Weatherly, the Co-directors and James H. Mauldin, Graduate Assistant, have devoted one-third time to research under this contract. Mr. Donald F. Eagle, a graduate student in physics, has assisted in the project work without pay while fulfilling the requirements for a graduate laboratory course. Mr. Eagle may be employed as a part-time graduate assistant during the coming quarter.

Fiscal: Expenditures during the quarter were as follows:

Salaries and Wages	$1601.37
Overhead	928.80
Supplies	590.59
Freight and Express	6.11
Travel	253.92
Total	$3380.79

Microwave Spectroscopy: Mr. Mauldin has continued with the work on the 85 Kc. square wave generator for the Stark modulating voltage. All the components have been received and it should be completed during the next quarter.

Nitrosyl Bromide: Results of the preliminary measurements on this molecule were reported at the New York meeting of the American Physical Society, January 27-29, 1955. Since that time the frequencies of the spectral lines of the $J=2\rightarrow 3$ transition have been remeasured but no appreciable differences were noted. The final report on this molecule will be postponed until the lines can be observed using a square wave Stark modulating voltage.

Nitryl Chloride: A sample of NO_2Cl has been prepared with the help of Dr. W. H. Eberhardt of the School of Chemistry. Approximately twenty spectral lines have been observed by letting the gas flow through the absorption cell cooled to dry ice temperature. Positive identification of the lines has not yet been made.

GEORGIA INSTITUTE OF TECHNOLOGY
ATLANTA, GEORGIA

SCHOOL OF PHYSICS

Status Report No. 7

DETERMINATION OF MOLECULAR CONSTANTS BY MICROWAVE AND RADIOFREQUENCY SPECTROSCOPY

Contractor:--

Georgia Tech Research Institute
Research Building
Georgia Institute of Technology
Atlanta, Georgia

Period:--

1 April 1955 to 30 June 1955

Project No.:--

OOR 1016

Contract No.:--

DA-01-009-ORD-353

Submitted by:--

T. L. Weatherly
Associate Professor

Joel Q. Williams
Associate Professor

Approved by:--

for Paul K. Calaway, Director
Engineering Experiment Station

Status Report No. 7

Determination of Molecular Constants

by

Microwave and Radiofrequency Spectroscopy

Contract No. DA-01-009-ORD-353

Personnel: During the quarter ending 30 June 1955, Joel Q. Williams and Thomas L. Weatherly, the co-directors and James H. Mauldin, Graduate Assistant, have devoted one-third of their time to research under this contract. Mr. Donald F. Eagle, a graduate student in physics has assisted without pay while fulfilling the requirements for a graduate laboratory course. Effective 1 July 1955 he will be employed as a Graduate Assistant for three-eights time. Mr. Larry Clayton, an advanced graduate student in physics will be employed effective 1 July 1955 as a Graduate Assistant for one-fifth time.

Mr. Mauldin received his Masters Degree in physics this June and is no longer connected with the project. The 85 Kc. square wave generator which he constructed for this project served as the topic of his thesis.

Fiscal: Expenditures during the quarter were as follows:

Salaries and wages	$1480.73
Overhead	858.83
Supplies	231.92
Total	$2571.48

Microwave Spectroscopy: The 85 Kc. square wave generator has been completed and tested by observation of the Stark components of the $J = 1 \rightarrow 2$ transition of carbonyl sulfide and the Stark components of the $J = 6$ restricted internal rotation line of methyl alcohol. In both cases the resolution and sensitivity were satisfactory.

The spectral lines of the $J = 2 \rightarrow 3$ transition of nitrosyl bromide have just been remeasured using square wave Stark modulation. The final calculations on this molecule will be made and a technical report written during the next quarter.

The observed lines of nitryl chloride mentioned in the last status report will be measured in the near future. The analysis of this spectrum has been assigned to Mr. Clayton who is a candidate for a Ph. D. degree in physics. If this analysis is successful it will be used as the topic for his thesis.

GEORGIA INSTITUTE OF TECHNOLOGY
ATLANTA, GEORGIA

SCHOOL OF PHYSICS

Status Report No. 8

DETERMINATION OF MOLECULAR CONSTANTS BY MICROWAVE AND RADIOFREQUENCY SPECTROSCOPY

Contractor:--

Georgia Tech Research Institute
Research Building
Georgia Institute of Technology
Atlanta, Georgia

Period:--

1 July 1955 to 30 September 1955

Project No.:--

OOR 1016

Contract No.:--

DA-01-009-ORD-353

Submitted by:--

T. L. Weatherly
Associate Professor

Joel Q. Williams
Associate Professor

Approved by:--

Paul K. Calaway, Director
Engineering Experiment Station

Status Report No. 8

Determination of Molecular Constants

by

Microwave and Radiofrequency Spectroscopy

Contract No. DA-01-009-ORD-353

Personnel: During the summer quarter ending 30 September, 1955, Joel Q. Williams and Thomas L. Weatherly, the co-directors, have devoted full time to research under this contract. Mr. Donald F. Eagle was employed 1 July, 1955, as a Graduate Assistant for three-eights time. Mr. Larry Clayton was employed 1 July, 1955, as a Graduate Assistant for one-fifth time. Both Mr. Eagle and Mr. Clayton are working toward advanced degrees in physics.

Fiscal: Expenditures during the quarter were as follows:

Salaries and Wages	$4,415.22
Overhead	2,560.83
Supplies	167.28
Total	7,143.33

Microwave Spectroscopy: Calculations based on the observed spectrum of nitrosyl bromide have been made. The rotational constants, the bromine quadrupole coupling constants, and the structure of the molecule were obtained. The results were reported in a technical report, and a paper entitled "Microwave Spectrum and Molecular Constants of Nitrosyl Bromide" was submitted for publication in the Physical Review. Additional calculations are being made to determine whether or not it will be possible to obtain the dipole moment from the Stark splitting of one of the absorption lines. Such calculations are necessarily difficult when they involve nearly degenerate rotational levels split by nuclear quadrupole coupling as in this case.

Frequency measurements of the observed lines of nitryl chloride have been made and an analysis of the spectrum is being attempted.

GEORGIA INSTITUTE OF TECHNOLOGY
ATLANTA, GEORGIA

SCHOOL OF PHYSICS

Status Report No. 9

DETERMINATION OF MOLECULAR CONSTANTS BY MICROWAVE AND RADIOFREQUENCY SPECTROSCOPY

Contractor:--

Georgia Tech Research Institute
Research Building
Georgia Institute of Technology
Atlanta, Georgia

Period:--

1 October 1955 to 31 December 1955

Project No.:--

OOR 1016

Contract No.:--

DA-01-009-ORD-353

Submitted by:--

T. L. Weatherly
Associate Professor

Joel Q. Williams
Associate Professor

Approved by:--

Paul K. Calaway, Director
Engineering Experiment Station

Status Report No. 9

Determination of Molecular Constants

by

Microwave and Radiofrequency Spectroscopy

Contract No. DA-01-009-ORD-353

Personnel: During the fall quarter ending 31 December 1955 the co-directors, Joel Q. Williams and T. L. Weatherly, have devoted one-third time to research under this contract. Mr. Donald F. Eagle and Mr. Larry Clayton were employed as graduate assistants for one-third time and one-fifth time respectively. Mr. Eagle will receive his master's degree in June, and Mr. Clayton is a candidate for a Ph. D. degree and will use his work on this project as a basis for his dissertation.

Fiscal: Expenditures during the quarter were as follows:

Salaries and Wages	$ 1855.30
Overhead	1076.08
Supplies	317.81
Freight and Express	6.77
Total	$ 3255.96

There is an unliquidated encumbrance of $600.51, leaving an unencumbered balance of $ 775.37 at the end of the period covered by this contract.

Research: During the quarter covered by this report Mr. Larry Clayton has made a number of changes in the components of the microwave spectrograph which have resulted in a considerable improvement in stability, sensitivity, and resolution of Stark Components. Investigation of the microwave spectrum of nitryl chloride (NO_2Cl) has continued with encouraging results. A calculation of the quadrupole splitting is now under way which should provide a positive identification of the observed spectral lines.

The calculations of the Stark splitting of the nitrosyl bromide (NOBr) absorption lines have not been completed. The work on nitrosyl bromide and nitryl chloride will be continued during the next quarter under the new contract.

A-128

Technical Report No. 1

DETERMINATION OF MOLECULAR CONSTANTS BY MICROWAVE AND

RADIO-FREQUENCY SPECTROSCOPY

Contractor: Georgia Tech Research Institute
Research Building
Georgia Institute of Technology
Project A-128

Department of Army Project No. 599-01-004

Ordnance Research and Development Project No. TB2-0001

OOR Project No. 1016

Contract No. DA-01-009-ORD-353

MICROWAVE SPECTRUM AND MOLECULAR CONSTANTS OF NITROSYL BROMIDE

by

T. L. Weatherly and Quitman Williams

Submitted 19 September 1955

(ABSTRACT)

The microwave spectrum of NOBr has been studied in the region 20,000 to 40,000 Mc/sec and an analysis made of the J = 2→3 transition. The following molecular constants were obtained.

	$NOBr^{79}$	$NOBr^{81}$
Rotational Constants (Mc/sec)		
A	83,340	83,340
B	3,747.24	3,722.49
C	3,586.00	3,563.34
Asymmetry Parameter		
b	-.001012	-.000998
Quadrupole Coupling Components (Mc/sec)		
χ_{aa}	388.3	325.5
χ_{bb}	-239.5	-200.2
χ_{cc}	-148.8	-125.3

The structural parameters obtained from these are d(N-O) = 1.15 A, d(N-Br) = 2.14 A, d(O-Br)= 2.81 A and ∠ Br-N-O = 114°. The interatomic distances are compared with electron diffraction results and a brief interpretation of the quadrupole coupling in terms of chemical bonds is given.

Introduction

The internuclear distances and bond angle of nitrosyl bromide have been measured by electron diffraction. J. A. Ketelaar and K. J. Palmer[1] report the values d(N-Br) = 2.14 ± .02 A, d(N-O) = 1.15 ± .04 A, d(O-Br) = 2.85 ± .02 A, and ∠ Br-N-O = 117° ± 3°. The moments of inertia for $NOBr^{81}$ calculated from this structure are $I_A = 9.39 \times 10^{-40}$ gm cm^2, $I_B = 230 \times 10^{-40}$ gm cm^2 and $I_C = 240 \times 10^{-40}$ gm cm^2 indicating that the molecule is an almost symmetric top. The rotational spectrum predicted on the basis of these moments consists of three groups of lines centered at approximately 21,400, 28,500, and 35,700 Mc/sec for the J = 2→3, 3→4, and 4→5 transitions respectively. Similarly the predicted spectrum for $NOBr^{79}$ in this region consists of three groups of lines which overlap the corresponding groups of $NOBr^{81}$. The observed lines fall into groups 400 to 700 Mc/sec higher in frequency than those predicted. This rough agreement between the observed and calculated spectra served as a preliminary identification of the J values involved in each transition. The observed spectrum is difficult to interpret due to the asymmetry of the molecule, the large quadrupole moments of the bromine nuclei, the presence of two isotopic species, and a complicated Stark effect. The present analysis is based primarily on the J = 2→3 transition.

Experimental

The sample of NOBr was prepared by admitting gaseous NO and Br_2 in the ratio 2 to 1 to a 1000 cc flask until a final pressure of 1 atmosphere was obtained. The mixture was then frozen with liquid nitrogen and the excess NO was pumped off. The NOBr was given off the remaining solid as its temperature was increased. This sample was allowed to flow through an absorption cell cooled to dry ice temperature.

The absorption lines were observed on the oscilloscope of a Stark modulated microwave spectrograph. The absorption cell consisted of X-band waveguide 18 feet

long with a brass strip mounted in the center as first described by Hughes and Wilson[2]. The Stark voltage was an 85 kc square wave of variable amplitude but zero-based so that one side of the square wave was held at ground potential. Frequencies were measured using a microwave frequency standard built by Scientific Associates of Atlanta, Georgia. It employs a 5 Mc/sec crystal controlled oscillator which may be zero-beat against the 5 or 10 Mc/sec signal from station WWV. The oscillator frequency is multiplied by vacuum tube circuits up to 2,160 Mc/sec and multiplied by a 1N26 silicon crystal to the microwave region. The frequency measurements were made in the manner described by Unterberger and Smith[3] with the exception that they were made in pairs by first sweeping the klystron from low to high frequency and then reversing the sweep voltage. The average of the two measurements was taken as the line frequency.

Analysis of Data

The observed and computed line frequencies are listed in Table I. The value of F in this table is obtained by the addition of the rotational quantum number J and the spin I = 3/2 of the bromine nucleus. The small quadrupole interaction of the nitrogen nucleus was expected to produce splittings of less than 1 Mc/sec and has been neglected. The rotational spectrum of NCBr for the J = 2→3 transition consists of five lines for each isotopic species as shown in Figure 1. Each of these lines is split into several components by the large bromine nuclear quadrupole interaction with the electric field gradient at the bromine nucleus giving the 28 lines of observable intensity listed in Table I.

Figure 1. Pure rotational spectrum for the J = 2→3 transition of $NCBr^{79}$.

Table I. Calculated and observed frequencies (Mc/sec) of the J = 2→3 transition of NOBr. The estimated errors of the observed frequencies are 0.25 Mc/sec.

Transition J	Transition F	$NOBr^{79}$ Calculated freq.	$NOBr^{79}$ Weighted average*	$NOBr^{79}$ Observed freq.	$NOBr^{81}$ Calculated freq.	$NOBr^{81}$ Weighted average*	$NOBr^{81}$ Observed freq.
$2_{-1}-3_{-2}$	5/2-5/2	21,743.36		21,742.93	21,606.47		21,606.22
	1/2-3/2	21,745.67		21,745.74	21,608.51		21,608.49
	7/2-9/2	21,747.78		21,747.91	21,610.24		21,609.91
	3/2-5/2	21,769.93		21,769.84	21,628.84		21,628.84
	5/2-7/2	21,772.04		21,771.95	21,630.58		21,630.32
$2_{-2}-3_{-3}$	5/2-7/2	21,994.15	21,994.17	21,993.86	21,852.62	21,852.64	21,852.23
	7/2-9/2	21,994.18			21,852.65		
	3/2-5/2	22,018.19	22,018.21	22,016.97	21,872.77	21,872.78	21,871.10
	1/2-3/2	22,018.23			21,872.80		
2_1-3_0	7/2-9/2	21,972.00			21,834.22		
	7/2-7/2	21,972.00			21,834.22		
	7/2-5/2	21,972.00	21,973.03	21,972.29	21,834.22	21,834.70	21,835.19
2_2-3_1	7/2-9/2	21,972.94			21,835.17		
	7/2-7/2	21,973.00			21,835.22		
	7/2-5/2	21,972.97			21,835.20		
2_1-3_0	3/2-3/2	21,994.74			21,857.47		
	3/2-5/2	21,999.74	22,000.21	22,001.07	21,857.47	21,857.95	21,858.69
2_2-3_1	3/2-3/2	22,000.64			21,858.39		
	3/2-5/2	22,000.70			21,858.44		
2_1-3_0	5/2-3/2	22,069.08			21,915.59		
	5/2-5/2	22,069.08			21,915.59		
	5/2-7/2	22,069.08	22,069.56	22,069.77	21,915.59	21,916.08	21,916.77
2_2-3_1	5/2-3/2	22,069.97			21,916.50		
	5/2-5/2	22,070.03			21,916.54		
	5/2-7/2	22,070.05			21,916.57		
2_0-3_{-1}	7/2-9/2	22,230.43		22,230.38	22,086.79		22,086.65
	1/2-3/2	22,233.93		22,233.60	22,089.69		22,089.42
	5/2-7/2	22,254.69		22,254.57	22,107.12		22,106.69
	3/2-5/2	22,258.20		22,258.34	22,110.03		22,110.25

* The calculated relative intensities were used for the weighting factors.

The quadrupole splitting of the observed lines was calculated by the first-order theory of Bragg[4]. For the initial calculations the electron distribution near the bromine nucleus was assumed to be symmetric about the N-Br bond axis. This resulted in a predicted spectrum in fairly close agreement with that observed, and the coupling constants reported previously[5]. Later measurements revealed the splitting of the $2_{-1} \rightarrow 3_{-2}$ and $2_{0} \rightarrow 3_{-1}$ lines shown in Table I and made possible a calculation of the diagonal components of the quadrupole coupling tensor with respect to the molecular principal axes. Bragg's theory was applied first by the use of his equation (8) and the tabulated line intensities of Cross, Hainer and King[6] making a linear interpolation. Because of the coarseness of the table of line intensities a second calculation was made using Bragg's equation (10) and the expansion coefficients $S_{K\tau}$ computed for a rotator with asymmetry parameter $b = 10^{-3}$. The difference in the spectra calculated by the two methods was almost insignificant. The spectrum predicted by the latter method is recorded in Table I. The coupling constants computed from the observed spectrum are listed in Table II, where $\chi_{aa} = eQ\,(\partial^2 V/\partial a^2)$, $\chi_{bb} = eq(\partial^2 V/\partial b^2)$, and $\chi_{cc} = eq(\partial^2 V/\partial c^2)$.

Table II. Bromine Quadrupole Coupling Constant.

	Br^{79}	Br^{81}
χ_{aa}	388.3 ± 2.9 Mc/sec	325.5 ± 2.9 Mc/sec
χ_{bb}	-239.5 ± 3.6	-200.2 ± 3.6
χ_{cc}	-148.8 ± 6.5	-125.3 ± 6.5

From the observed spectrum and the calculated quadrupole splittings the rotational spectrum without quadrupole splitting was determined. The rotational constants were then calculated by the theory of Wang[7]. According to this theory

the rotational energies of an asymmetric top molecule are given by

$$F(J_\tau) = (1/2)\ (B+C)J(J+1) + \left[A - 1/2\ (B+C)\right]\ W_\tau, \qquad (1)$$

where A, B, and C, are the rotational constants, and J is the rotational quantum number. The 2J + 1 values of W_τ are obtained as solutions to algebraic equations in terms of the asymmetry parameter

$$b = -\frac{(B-C)}{2A-(B+C)}.$$

For NOBr b is approximately 10^{-3} and it is convenient to expand the values of W_τ in terms of b. The values of W_τ which are important to this analysis are:

for J = 2	for J = 3
$W_{+1} = 4$	$W_0 = 4$
$W_0 = 1-3b$	$W_{-1} = 1-6b - \frac{15}{8} b^2 + \frac{45}{32} b^3 + \ldots$
$W_{-1} = 1 + 3b$	$W_{-2} = 1+6b - \frac{15}{8} b^2 - \frac{45}{32} b^3 + \ldots$

These values of W_τ when substituted into equation (1) give for the frequency of the center line of Figure 1

$$\nu\ (2_{+1} - 3_0) = 3(B + C)$$

and for the frequency difference between the upper and lower lines

$$\nu\ (2_0 - 3_{-1}) - \nu(2_{-1} - 3_{-2}) = 3(B-C)\left[1 - \frac{15}{32} b^2 + \ldots\right].$$

Since b^2 is approximately 10^{-6} this term and all higher order terms of the last equation may be neglected and approximate values of the rotational constants B and C may be determined from the three lines identified in Figure 1. The approximate values of B and C were then adjusted slightly to obtain the best fit of observed and calculated spectra. The resulting rotational constants are listed in Table III. The constant A in this table was determined from the relation $I_C = I_A + I_B$ for a planar molecule. Although this relationship is not entirely accurate for a vibrating molecule the error introduced should be small compared to the limits placed on this constant in Table III.

Table III. Rotational Constants for NOBr.

	$NOBr^{79}$	$NOBr^{81}$
A	83,340 ± 104 Mc/sec	83,340 ± 117 Mc/sec
B	3,747.24 ± .10	3,722.49 ± .11
C	3,586.00 ± .10	3,563.34 ± .11
Asymmetry Parameter		
b	-.001012	-.000998

The rotational constants of two isotopic species of NOBr along with a knowledge of the general shape of the molecule provide more than enough data for computing the structure. In order to make use of all the data the structural parameters were calculated by two different methods which prove to be almost independent. The first has been described by J. Kraitchman[8] and makes use of the moments of inertia I_A^{79}, I_B^{79}, I_A^{81}, and I_B^{81}, the factor of major importance being the difference $I_B^{81} - I_B^{79}$.

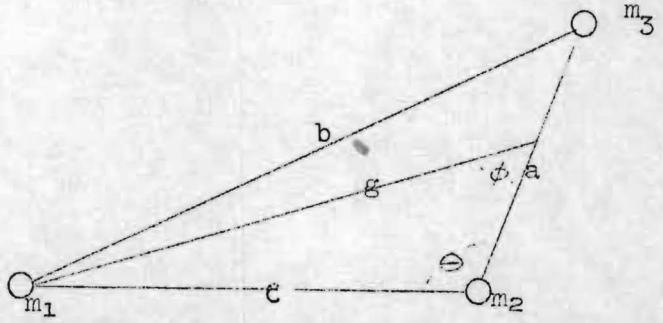


Figure 2. Parameters used in determining the molecular structure. The line g joins m_1 with the center of mass of m_2 and m_3.

A second solution utilizing different data may be obtained by computing the momental dyadic in terms of a, b, c, and θ of Figure 2 and transforming to principal axes. From the secular determinant one obtains the equations

$$I_C = (m_2 m_3 a^2 + m_1 m_3 b^2 + m_1 m_2 c^2)/M$$

$$I_A I_B = m_1 m_2 m_3 a^2 c^2 \sin^2\theta / M$$

where m_i are the respective masses and M is the total mass. By applying the above equations to each isotopic species one gets for the structural constants of Figure 2

$$a^2 = \frac{m_1' \, MI_C - m_1 M' I_C'}{(m_1' - m_1) m_2 m_3}$$

$$g^2 = \frac{M'M(I_C' - I_C)}{(m_2 + m_3)2\,(m_1' - m_1)}$$

$$\sin^2\phi = \frac{M\, I_A\, I_B}{m_1 m_2 m_3 a^2 g^2}$$

where a is the distance between atoms 2 and 3, g is the distance from 1 to the center of mass of 2 and 3, and ϕ is the angle between g and a. Isotopic substitution is made for atom 1 and the primed quantities refer to the molecule containing the heavier isotope. The bond distances and angle may be obtained from a, g, and ϕ by the laws of trigonometry. The values of a, b, c, and θ obtained by this method depend on I_A^{79}, I_B^{79}, I_C^{79}, and I_C^{81} with I_C^{79} and I_C^{81} having the greatest influence on the results.

Since the accuracy of the first method depends on a precise measurement of I_B^{79} and I_B^{81} and the accuracy of the second method depends on a precise measurement of I_C^{79} and I_C^{81} both methods were used for determining a, b, and c. The results of the two methods agreed to within .01 A for all distances. The average values obtained by the two methods are recorded in Table IV.

Table IV. Structure of NOBr from microwave data.

d (N-O)	= 1.15 ± .06 A
d (N-Br)	= 2.14 ± .06 A
d (Br-O)	= 2.81 ± .04 A
∠ Br-N-O	= 114°

Results

The observed lines in Table I varied in width from 1 to 3 Mc/sec. Calculated lines separated by less than 1 Mc/sec have been weighted according to their relative intensities and averaged. In most cases this weighted average agrees with the observed line to within less than .5 Mc/sec, the most notable exceptions being the $2_{-2} \rightarrow 3_{-3}$ transition in each molecule. These lines, unlike the others, require a very high Stark voltage for detection, and it seems likely that they were displaced to lower frequencies by imcompletely separated Stark components.

The structural parameters listed in Table IV differ from the electron diffraction results only in the O-Br distance and the bond angle. Unfortunately the present analysis does not give structural constants as accurately as electron diffraction. The geometry of the molecule is such that a change in one distance can be compensated by proper adjustment of the two remaining distances with very little effect on the spectrum. However, if d(N-O) = 1.15 A and d(N-Br) = 2.14 A as measured by electron diffraction and calculated from the spectrum, then d(O-Br) must be less than 2.83 A. Therefore it would seem that the electron diffraction measurement of this distance is a little large.

The ratio of the Br^{79} to Br^{81} quadrupole coupling components from Table II is 1.193 $\pm$ .020 for the components χ_{aa} and 1.196 $\pm$ .040 for the components χ_{bb}. These ratios are in good agreement with coupling constant ratios obtained from pure quadrupole resonance in solid bromine compounds.

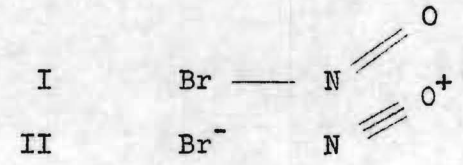
In order to increase the usefulness of the bromine quadrupole coupling tensor for analysis of the N-Br bond it has been transformed to a coordinate system with z axis oriented along the bond direction, x axis in the plane of the molecule and y axis perpendicular to this plane. Such a transformation requires the knowledge of the component χ_{ab} as well as the diagonal elements listed in Table II. Goldstein[9] has pointed out that this off-diagonal element

may be computed if we assume that the xyz axes are principal axes of the quadrupole coupling tensor. Following this suggestion the value of χ_{xy} obtained from the tensor transformation was set equal to zero and the resulting equation solved for χ_{ab}. The transformation to xyz axes was then made in the usual way. The diagonal elements in Mc/sec with respect to this set of axes are

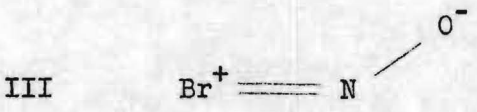
	$NOBr^{79}$	$NOBr^{81}$
χ_{xx}	-290.2	-242.6
χ_{yy}	-148.8	-125.3
χ_{zz}	+439.0	+367.9

The asymmetry parameter $\eta = (\chi_{xx} - \chi_{yy})/\chi_{zz}$ is -0.322 for $NOBr^{79}$ and -0.319 for $NOBr^{81}$.

Ketelaar and Palmer[1] have suggested for NOBr the two structures



each making a 50% contribution. The second of these was introduced to explain the large N-Br distance of 2.14 A compared to a sum of covalent radii 1.84 A. The large asymmetry parameter $\eta \approx -0.320$ suggests an appreciable contribution of a third structure,



The importance of this structure in bond formation is related to the quantity

$$\delta = \frac{\chi_{xx} - \chi_{yy}}{-(3/2)(eqQ)_{atomic}}$$

defined by Goldstein[9]. This quantity is a measure of the number of electronic charges lost by the bromine in double bond formation. Assuming an $(eqQ)_{atomic}$ for Br^{79} of 769.6 Mc/sec[10] the value of δ becomes 0.12 indicating roughly a

12% contribution of structure III. The individual contributions of structures I and II may be estimated from χ_{zz} by using the method of Townes and Dailey[11] assuming a pure p covalent bond in structure I. The resulting contributions are 49% for structure I and 39% for structure II. It should be emphasized that the above estimates of the percent contribution of each structure are very crude, and will undoubtedly require revision as more is learned concerning the relation of quadrupole coupling to chemical bonds.

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